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(54) Catalysts and process for producing olefin polymers.

(57) The invention relates to novel catalysts for polymerization of ethylene or α -olefins, comprising a metallocene, an organoaluminum compound an ionic compound, and a boron compound, or comprising an ionic metallocene, an organoaluminum compound and a boron compound, and a process for polymerization of ethylene or α -olefins using the above catalysts.

EP 0 570 982 A1

The present invention relates to a process for producing olefin polymers by use of a polymerization catalyst comprising a metallocene, an organoaluminum compound, and an ionic compound.

The present invention also relates to a process for producing olefin polymers by use of a polymerization catalyst comprising an ionic metallocene and an organoaluminum compound.

5 The polymerization of ethylene or an α -olefin by a low-pressure Ziegler process is well known in the art. The catalyst therefor is prepared by mixing an organometallic compound or a hydride of an element of the 1A to 3A Group of the Periodic Table with a compound of a transition metal (an element of the 3B to 2B Group of the Periodic Table), and treating the mixture in suspension or solution or in the absence of a diluent or a solvent.

10 Known special kinds of catalysts active for olefin polymerization include combinations of aluminoxane with a cyclopentadienyl derivative of a metal of the 4B Group, namely titanium, zirconium, and hafnium. Such catalysts are disclosed in the literature "Ziegler-Natta catalyst and polymerization", Academic Press, New York (1979); Adv. Organomet. Chem. 1899 (1980); and so forth. Such catalysts advantageously exhibit high catalytic activity and are capable of producing stereoregular polyolefins. However, these catalyst have
15 not been used in industrial polymerization, mainly because the aluminoxane cannot readily be synthesized in a reproducible manner and therefore also the catalysts and the polymers cannot be prepared reproducibly.

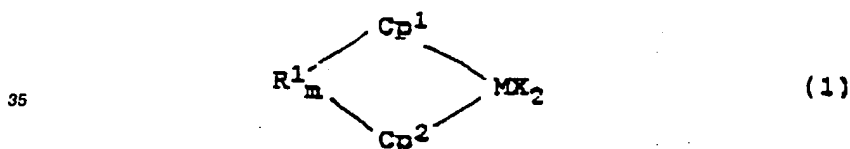
A catalyst which offsets such problems is disclosed in JP-A-3-207704, which describes a bis-(cyclopentadienyl)metal compound prepared by reaction of a metallocene with an ionic compound and the
20 use of the resulting complex as a polymerization catalyst. This catalyst, however, is not satisfactory in the catalyst activity.

Thus, it is an object of the present invention to solve the above problems of the olefin polymerization catalyst employing a metallocene and an organoaluminum compound, and to provide a novel catalyst for polymerization of ethylene or α -olefin.

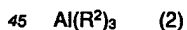
25 Another object of the present invention is to provide a process for polymerization of ethylene or α -olefin by use of the above novel catalyst system.

The first object has been achieved by an olefin polymerization catalyst system which comprises a metallocene compound (A), an organoaluminum compound (B), and an ionic compound (C) as catalyst components:

30 the metallocene compound (A) being represented by the general formula (1) below:



where Cp^1 , and Cp^2 are independently a substituted or unsubstituted cyclopentadienyl groups; R^1 is an
40 alkylene group having 1 to 20 carbons, a dialkylsilylene group, a dialkylgermanylen group, an alkylphosphindiyl group, or an alkylimino group which crosslink Cp^1 and Cp^2 ; m is 0 or 1; M is titanium, zirconium, or hafnium; and X is fluorine, chlorine, bromine, iodine, an alkyl group, or an aryl group; the organoaluminum compound (B) being represented by the general formula (2):



where each or the R^2 groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, or an aryl group, and at least or one the R^2 groups is an alkyl group; and the ionic compound (C) being
50 represented by the general formula (3) below:



where $[C]$ is a cation and $[A]$ is an anion;

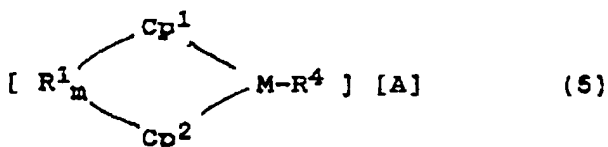
the catalyst system further containing a boron compound (D) represented by the general formula (4) below:



where each of the R^3 groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, or an

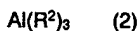
aryl group, in an amount of from 0.01 mol to 0.8 mol per mol of the metallocene compound (A).

This object is also achieved by an olefin polymerisation catalyst which comprises an ionic metallocene compound (a), and an organoaluminum compound (b) as catalyst components: the ionic metallocene compound (a) being represented by the general formula (5) below:



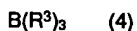
where Cp¹, Cp², R¹, m, and M are the same as defined in the formula (1), R⁴ is an alkyl group or an aryl group, and [A] is an anion; and

the organoaluminum compound (b) being represented by the general formula (2):



where R² is as defined above, and at least one of the R² groups is an alkyl group:

the catalyst system further containing a boron compound represented by the general formula (4) below:

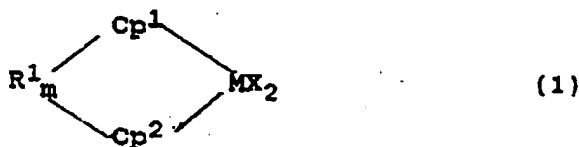


where R³ is as defined above; in an amount of from 0.01 mol to 0.8 mol per mol of the ionic metallocene compound (a).

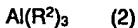
The second object of the present invention is achieved by the provision of a process for the polymerization of ethylene or α -olefin employing the aforementioned catalyst system comprising a metallocene, an organoaluminum compound, an ionic compound, and a boron compound, or a catalyst system comprising an ionic metallocene, an organoaluminum compound, and a boron compound.

The process for producing an olefin polymer, according to an aspect of the present invention, employs a polymerization catalyst system which comprises a metallocene compound (A), an organoaluminum compound (B), and an ionic compound (C) as catalyst components:

the metallocene compound (A) being represented by the general formula (1) below:



where Cp¹, and Cp² are independently a substituted or unsubstituted cyclopentadienyl group; R¹ is an alkylene group having 1 to 20 carbons, a dialkylsilylene group, a dialkylgermylene group, an alkylphosphindiy group, or an alkylimino group which crosslink Cp¹ and Cp²; m is 0 or 1; M is titanium, zirconium, or hafnium; and X is fluorine, chlorine, bromine, iodine, an alkyl group, or an aryl group; the organoaluminum compound (B) being represented by the general formula (2):

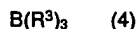


where each of the R² groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, Or an aryl group, and at least of one the R² groups is an alkyl group; and the ionic compound (C) being represented by the general formula (3) below:



where [C] is a cation and [A] is an anion;

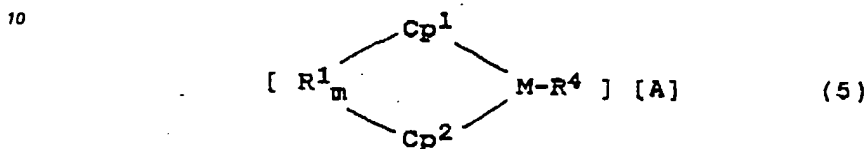
the catalyst system further containing a boron compound (D) represented by the general formula (4) below:



where each of the R^3 groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, or an aryl group, in an amount of from 0.01 mol to 0.8 mol per mol of the metallocene compound (A).

5 The process for producing an olefin polymer, according to another aspect of the present invention, employs an olefin polymerization catalyst comprises an ionic metallocene compound (a), and an organoaluminum compound (b) as catalyst components:

the ionic metallocene compound (a) being represented by the general formula (5) below:



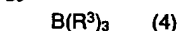
15 where Cp^1 , Cp^2 , R^1 , m , and M are the same as defined in the formula (1), R^4 is an alkyl group or an aryl group, and $[A]$ is an anion: and

the organoaluminum compound (b) being represented by the general formula (2):



where R^2 is as defined above, and at least one of the R^2 groups is an alkyl group;

the catalyst system further containing a boron compound represented by the general formula (4) below;



where R^3 is as defined above; in an amount of from 0.01 mol to 0.8 mol per mol of the ionic metallocene compound (a).

30 The metallocene compound (A) used in the present invention is represented by the general formula (1).

Specific examples thereof include

bis(cyclopentadienyl)titanium dichloride,

bis(pentamethylcyclopentadienyl)titanium dichloride,

ethylenebis(indenyl)titanium dichloride,

35 ethylenebis(tetrahydroindenyl)titanium dichloride,

isopropylidene(cyclopentadienyl)(fluorenyl)titanium dichloride,

dimethylsilylbis(methylcyclopentadienyl)titanium dichloride,

dimethylsilylbis(2,4-dimethylcyclopentadienyl)titanium dichloride,

bis(cyclopentadienyl)zirconium dichloride,

40 bis(pentamethylcyclopentadienyl)zirconium dichloride,

ethylenebis(indenyl)zirconium dichloride,

ethylenebis(tetrahydroindenyl)zirconium dichloride,

isopropylidene(cyclopentadienyl)(fluorenyl)zirconium dichloride,

dimethylsilylbis(methylcyclopentadienyl)zirconium dichloride,

45 dimethylsilylbis(2,4-dimethylcyclopentadienyl)zirconium dichloride,

bis(cyclopentadienyl)hafnium dichloride,

bis(pentamethylcyclopentadienyl)hafnium dichloride,

ethylenebis(indenyl)hafnium dichloride,

ethylenebis(tetrahydroindenyl)hafnium dichloride,

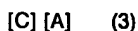
50 isopropylidene(cyclopentadienyl)(fluorenyl)hafnium dichloride,

dimethylsilylbis(methylcyclopentadienyl)hafnium dichloride,

dimethylsilylbis(2,4-dimethylcyclopentadienyl)hafnium dichloride. Specific compounds having other substituents within the scope of the invention may also be effectively used.

The ionic metallocene compound (a) employed in the present invention may be prepared, for example, 55 by mixing a neutral derivative of a metallocene with an ionic compound (c) in a solvent and, if desired, recovering the product. The molar ratio of the neutral metallocene derivativ to the ionizable ionic compound used therefore is preferably in the range of from 1:0.2 to 1:100, more preferably from 1:1 to 1:10.

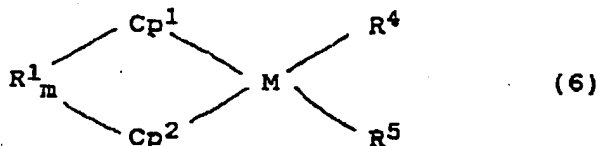
The ionic compound (c) is represented by the general formula (3) below



5 where [C] is a cation and [A] is an anion.

The solvent used in the above reaction includes toluene, hexane, and methylene chloride, but is not limited thereto.

The neutral metallocene compound used in the preparation of the ionic metallocene compound of the present invention is represented by the general formula (6) below:



wherein Cp¹, Cp², R¹, m, and M are as defined in the general formula (1) or (5), and R⁵ is hydrogen, a halogen, an amide group, or an alkyl group.

20 The specific examples of the neutral metallocene compound include

bis(cyclopentadienyl)titaniumdimethyl,
bis(pentamethylcyclopentadienyl)titaniumdimethyl,
ethylenebis(indenyl)titaniumdimethyl,
ethylenebis(tetrahydroindenyl)titaniumdimethyl,
25 isopropylidene(cyclopentadienyl)(fluorenyl)titaniumdimethyl,
dimethylsilylbis(methylcyclopentadienyl)titaniumdimethyl,
dimethylsilylbis(2,4-dimethylcyclopentadienyl)titaniumdimethyl,
bis(cyclopentadienyl)zirconiumdimethyl,
bis(pentamethylcyclopentadienyl)zirconiumdimethyl,
30 ethylenebis(indenyl)zirconiumdimethyl,
ethylenebis(tetrahydroindenyl)zirconiumdimethyl,
isopropylidene(cyclopentadienyl)(fluorenyl)zirconium-dimethylsilylbis(methylcyclopentadienyl)-
zirconiumdimethyl,
dimethylsilylbis(2,4-dimethylcyclopentadienyl)zirconiumdimethyl,
35 bis(cyclopentadienyl)hafniumdimethyl,
bis(pentamethylcyclopentadienyl)hafniumdimethyl,
ethylenebis(indenyl)hafniumdimethyl,
ethylenebis(tetrahydroindenyl)hafniumdimethyl,
isopropylidene(cyclopentadienyl)(fluorenyl)hafniumdimethyl,
40 dimethylsilylbis(methylcyclopentadienyl)hafniumdimethyl,
and dimethylsilylbis(2,4-dimethylcyclopentadienyl)hafniumdimethyl. Specific compounds having other substituents within the scope of the invention may also be effectively used.

The organoaluminum compound (B) or (b) is represented by the general formula (2). Specific examples thereof include trimethylaluminum, triethylaluminum, triisopropylaluminum, tri(n-propyl)aluminum, 45 triisobutylaluminum, tri(n-butyl)aluminum, tri(n-hexyl)aluminum, tri(n-octyl)aluminum, dimethylaluminum chloride, diethylaluminum chloride, diisopropylaluminum chloride, di(n-propyl)aluminum chloride, diisobutylaluminum chloride, di(n-butyl)aluminum chloride, dimethylaluminum ethoxide, diethylaluminum ethoxide, diisopropylaluminum ethoxide, di(n-propyl)aluminum ethoxide, diisobutylaluminum ethoxide, di(n-butyl)aluminum ethoxide, dimethylaluminum hydride, diethylaluminum hydride, diisopropylaluminum 50 hydride, di(n-propyl)aluminum hydride, diisobutylaluminum hydride, and di(n-butyl)aluminum hydride.

The ionic compound (C) or (c) is represented by the general formula (3). It is preferred that the ionic compound readily dissociates. The specific examples thereof include tri(n-butyl)ammonium tetrakis(p-tolyl)-borate, tri(n-butyl)ammonium tetrakis(m-tolyl)borate, tri(n-butyl)ammonium tetrakis(2,4-dimethylphenyl)-borate, tri(n-butyl)ammonium tetrakis(3,5-dimethylphenyl)borate, tri(n-butyl)ammonium tetrakis- 55 (pentafluorophenyl)borate, N,N-dimethylanilinium tetrakis(p-tolyl)borate, N,N-dimethylanilinium tetrakis(m-tolyl)borate, N,N-dimethylanilinium tetrakis(2,4-dimethylphenyl)borate, N,N-dimethylanilinium tetrakis(3,5-dimethylphenyl)borate, N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, triphenylcarbenium tetrakis(p-tolyl)borate, triphenylcarbenium tetrakis(m-tolyl)borate, triphenylcarbenium tetrakis(2,4-dimethylphenyl)-

borate, triphenylcarbenium tetrakis(3,5-dimethylphenyl)borate, triphenylcarb nium tetrakis-(pentafluorophenyl)borate, tropylium tetrakis(p-tolyl)borate, tropylium tetrakis(m-tolyl)borate, tropylium tetrakis(2,4-dimethylphenyl)borate, tropylium tetrakis(3,5-dimethylphenyl)borate, and tropylium tetrakis-(pentafluorophenyl)borate.

5 The boron compound (D) is represented by the general formula (4). The specific examples thereof include trifluoroborane, trichloroborane, tribromoborane, trimethylborane, triethylborane, triisopropylborane, tri(n-propyl)borane, triisobutylborane, tri(n-butyl)borane, triphenylborane, and tri(pentafluorophenyl)borane.

The organoaluminum compound in the present invention is used preferably at a concentration of from 10^{-5} mol/l to 10^{-3} mol/l.

10 The olefin specifically includes α -olefins such as ethylene, propylene, 1-butene, 4-methyl-1-pentene, 1-hexane, and 1-octene. Also a mixture of two or more of the olefins may be polymerized. Further, the olefin can be copolymerized with a conjugated or non-conjugated diene such as butadiene, 1,6-hexadiene, 1,4-pentadiene, 1,7-octadiene, 1,8-nonadiene, and 1,9-decadiene; styrene; or a cyclic olefin such as cyclopropene, cyclohexene, norbornene, and dicyclopentadiene.

15 The polymerization of olefins according to the present invention is conducted by any known process for olefin polymerization with a metallocene compound. The polymerization is conducted, for example, in bulk, in a slurry, or in a gas phase at a temperature of from -80°C to 250°C , preferably from 25°C to 80°C .

In the first aspect of the present invention, the olefin is polymerized, for example, by mixing the metallocene compound (A) and the organoaluminum compound (B) with an olefin, and the ionic compound
20 (C) containing the boron compound (D) is brought into contact with the above mixture. In the olefin polymerization, the molar ratio of the metallocene compound (A) to the ionic compound (C) is normally in the range of from 1:0.2 to 1:100, preferably from 1:1 to 1:10. The boron compound (D) is preferably added in an amount of from 0.01 mol to 0.8 mol, more preferably from 0.05 mol to 0.5 mol per mol of the metallocene compound (A). Thereby the activity of the catalyst system is greatly improved. On the contrary,
25 if the boron compound (D) is used in an amount of less than 0.01 mol, or more than 0.8 mol per mol at the metallocene compound (A), the catalyst activity is extremely low.

In the second aspect of the present invention, the olefin is polymerized, for example, by preparing an ionic metallocene compound (a) by mixing a neutral metallocene derivative with an ionic compound in a solvent, adding thereto a boron compound, and bringing the mixture into contact with a mixture of an
30 organoaluminum compound (b) and an olefin. In the olefin polymerization, the boron compound is preferably added in an amount of from 0.01 mol to 0.8 mol, more preferably from 0.05 mol to 0.5 mol per mol of the ionic metallocene compound (a). Thereby the activity of the catalyst system is greatly improved. On the contrary, if the boron compound is used in an amount of less than 0.01 mol, or more than 0.8 mol per mol of the ionic metallocene compound (a), the catalyst activity is extremely low.

35 The present invention is described in more detail by reference to examples without limiting the invention in any way.

Example 1

40 In a 2-liter autoclave, 500 ml of toluene was placed. Thereto 0.68 mmol of triethylaluminum was added, and the mixture was stirred for 10 minutes. To this solution, a solution of $1.3\text{ }\mu\text{mol}$ of ethylenebis(indenyl)-zirconium dichloride in 1 ml of toluene was added, and the mixture was stirred for 20 minutes. Then 500 ml of propylene was introduced, and the mixture was stirred for 10 minutes. Further, $1.3\text{ }\mu\text{mol}$ of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate and $0.13\text{ }\mu\text{mol}$ of tris(pentafluorophenyl)borane were
45 pressed into the autoclave with 10 ml of toluene, and polymerization was allowed to proceed at 40°C for one hour. The reaction product was dried in vacuo at about 70°C for 6 hours. Thus 160 g of propylene polymer was obtained.

Comparative Example 1

50 Polymerization was conducted in the same manner as in Example 1 except that tris(pentafluorophenyl)borane was not added. Thereby 95 g of propylene polymer was obtained.

Comparative Example 2

55 Polymerization was conducted in the sam manner as in Example 1 except that the amount of tris-(pentafluorophenyl)borane was changed to $1.3\text{ }\mu\text{mol}$. Thereby 21 g of propylene polymer was obtained.

Example 2

In a 2-liter autoclave, 500 ml of toluene was placed. Thereto 0.66 mmol of triethylaluminum was added, and the mixture was stirred for 10 minutes. To this solution, a solution of 5 μ mol of isopropylidene-(cyclopentadienyl)(fluorenyl)zirconium dichloride in 1 ml of toluene was added, and the mixture was stirred for 20 minutes. Then 500 ml of propylene was introduced thereto, and the mixture was stirred for 10 minutes. Further, 6.6 μ mol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate and 0.66 μ mol of tris-(pentafluorophenyl)borane were pressed into the autoclave with 10 ml of toluene, and polymerization was allowed to proceed at 40 °C for one hour. The reaction product was dried in vacuo at about 70 °C for 6 hours. Thus 95 g of propylene polymer was obtained.

Comparative Example 3

Polymerization was conducted in the same manner as in Example 2 except that tris(pentafluorophenyl)borane was not added. Thereby 20 g of propylene polymer was obtained.

Comparative Example 4

Polymerization was conducted in the same manner as in Example 2 except that the amount of tris-(pentafluorophenyl)borane was changed to 6.6 μ mol. Thereby 15 g of propylene polymer was obtained.

Example 3

A solution of 0.66 mmol triethylaluminum in 5 ml of toluene was placed in a 2-liter autoclave as the reactor. The temperature of the reactor was controlled to be at 70 °C. Therein, 1.4 liters of propylene was introduced, and the mixture was stirred at a rate of 1200 rpm for 10 minutes.

6.6 μ mol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate and 0.66 μ mol of tris-(pentafluorophenyl)borane were dissolved in 10 ml of toluene. Separately, 5 μ mol of ethylenebis(indenyl)zirconiumdimethyl was dissolved in 10 ml of toluene. These solutions were mixed and stirred at room temperature for 5 minutes.

The resulting catalyst mixture was charged into the reactor with nitrogen pressure. Thereby the temperature in the reactor rose up to 75 °C. At the end of the polymerization reaction, the reactor was cooled, and the unreacted propylene gas discharged from the reactor. The reaction product was dried in vacuo at about 70 °C for 6 hours. Thus 695 g of propylene polymer was obtained.

Comparative Example 5

Polymerization was conducted in the same manner as in Example 3 except that tris(pentafluorophenyl)borane was not added. Thereby 116 g of propylene polymer was obtained.

Comparative Example 6

Polymerization was conducted in the same manner as in Example 3 except that the amount of tris-(pentafluorophenyl)borane was changed to 6.6 μ mol. Thereby 25 g of propylene polymer was obtained.

Example 4

A solution of 0.66 mmol triethylaluminum in 5 ml of toluene was placed in a 2-liter autoclave as the reactor. The temperature of the reactor was controlled to be at 70 °C. Therein, 1.4 liters of propylene was introduced, and the mixture was stirred at a rate of 1200 rpm for 10 minutes.

72 μ mol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate and 7.2 μ mol of tris-(pentafluorophenyl)borane were dissolved in 10 ml of toluene. Separately, 55 μ mol of isopropylidene-(cyclopentadienyl)(fluorenyl)zirconiumdimethyl was dissolved in 10 ml of toluene. These solutions were mixed and stirred at room temperature for 5 minutes.

The resulting catalyst mixture was charged into the reactor with nitrogen pressure. Thereby the temperature in the reactor rose up to 75 °C. At the end of the polymerization reaction, the reactor was cooled, and the unreacted propylene was discharged from the reactor. The reaction product was dried in vacuo at about 70 °C for 6 hours. Thus 410 g of propylene polymer was obtained.

Comparative Example 7

Polymerization was conducted in the same manner as in Example 4 except that tris(pentafluorophenyl)-borane was not added. Thereby 90 g of propylene polymer was obtained.

Comparative Example 8

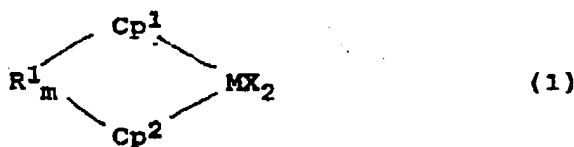
Polymerization was conducted in the same manner as in Example 4 except that the amount of tris-(pentafluorophenyl)borane was changed to 72 μ mol. Thereby 45 g of propylene polymer was obtained.

As described above, olefin polymers were produced with high efficiency with a high catalyst activity by use of a catalyst comprising a metallocene compound, an organoaluminum compound, and an ionic compound together with a boron compound, or a catalyst comprising an ionic metallocene compound, an organoaluminum compound, and a boron compound.

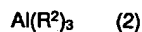
Claims

1. A process for producing in olefin polymer by use of a polymerization catalyst system, which comprises a metallocene compound (A), an organoaluminum compound (B), and an ionic compound (C) as catalyst components:

the metallocene compound (A) being represented by the general formula (1) below:



where Cp^1 , and Cp^2 are independently a substituted or unsubstituted cyclopentadienyl group; R^1 is an alkylene group having 1 to 20 carbons, a dialkylsilylene group, a dialkylgermanylene group, an alkylphosphindiy group, or an alkylimino group which crosslink Cp^1 and Cp^2 ; m is 0 or 1; M is titanium, zirconium, or hafnium; and X is fluorine, chlorine, bromine, iodine, an alkyl group, or an aryl group; the organoaluminum compound (B) being represented by the general formula (2):

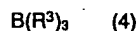


where each of the R^2 groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, or an aryl group, and at least of one of the R^2 groups is an alkyl group; and the ionic compound (C) being represented by the general formula (3) below:



where $[\text{C}]$ is a cation and $[\text{A}]$ is an anion;

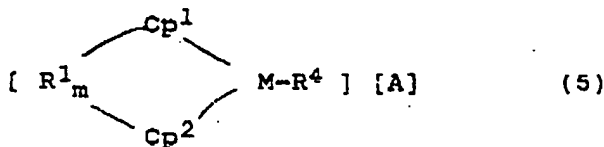
the catalyst system further containing a boron compound (D) represented by the general formula (4) below:



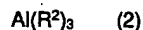
where each of the R^3 groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, or an aryl group, in an amount of from 0.01 mol to 0.8 mol per mol of the metallocene compound (A).

2. A process for producing an olefin polymer according to claim 1, wherein the catalyst system contains the boron compound (D) in an amount of from 0.05 mol to 0.5 mol per mol of the metallocene compound (A).
3. A process for producing an olefin polymer according to claim 1 or 2, wherein the metallocene compound (A) and the organoaluminum compound (B) are mixed with the olefin, and the mixture is brought into contact with the ionic compound (C) containing the boron compound (D).

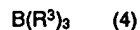
4. A process for producing an olefin polymer by use of a polymerization catalyst system, which comprises an ionic metallocene compound (a), and an organoaluminum compound (b) as catalyst components: the ionic metallocene compound (a) being represented by the general formula (5) below:



where Cp^1 , and Cp^2 are independently a substituted or unsubstituted cyclopentadienyl group; R^1 is an alkylene group, a dialkylsilylene group, 2 dialkylgermanylenes group, an alkylphosphindiyl group, or an alkylimino group, R^1 having 1 to 20 carbons and crosslinking Cp^1 and Cp^2 ; m is 0 or 1; R^4 is an alkyl group or an aryl group; M is titanium zirconium, or hafnium; and $[\text{A}]$ is an anion; and the organoaluminum compound (b) being represented by the general formula (2):

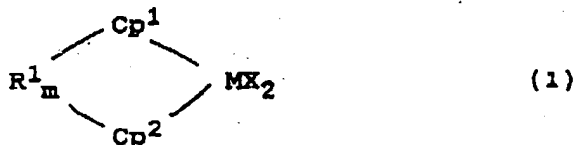


where each of the R^2 groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, or an aryl group, and at least one of the R^2 groups is an alkyl group; the catalyst system further containing a boron compound represented by the general formula (4) below:



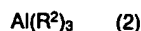
where each of the R^3 groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, or an aryl group, in an amount of from 0.01 mol to 0.8 mol per mol of the ionic metallocene compound (a).

5. A process for producing an olefin polymer according to claim 4, wherein the catalyst system contains the boron compound in an amount of from 0.05 mol to 0.5 mol per mol of the ionic metallocene compound (A).
6. A process for producing an olefin polymer according to claim 4 or 5, wherein the ionic metallocene compound (a) is added to the boron compound, and the resulting mixture is brought into contact with the organoaluminum compound and the olefin.
7. A process for producing an olefin polymer according to any of claims 1 to 6, wherein the boron compound is selected from trifluoroborane, trichloroborane, tribromoborane, triphenylborane, and tris(pentafluorophenyl)borane.
8. A process for producing an olefin polymer according to any of claims 1 to 7, wherein the olefin is selected from ethylene, propylene, 1-butene, 4-methyl-1-pentene, 1-hexene, and 1-octene.
9. A catalyst for polymerization of an olefin, which comprises a metallocene compound (A), an organoaluminum compound (B), and an ionic compound (C) as catalyst components: the metallocene compound (A) being represented by the general formula (1) below:



where Cp^1 , and Cp^2 are independently a substituted or unsubstituted cyclopentadienyl group; R^1 is an alkylene group having 1 to 20 carbons, a dialkylsilylene group, a dialkylgermanylenes group, an alkylphosphindiyl group, or an alkylimino group which crosslink Cp^1 and Cp^2 ; m is 0 or 1; M is titanium, zirconium, or hafnium; and X is fluorine, chlorine, bromine, iodine, an alkyl group, or an aryl group; the

organoaluminum compound (B) being represented by the general formula (2):

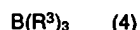


where each of the R^2 groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, or an aryl group, and at least one of the R^2 groups is an alkyl group; and the ionic compound (C) being represented by the general formula (3) below:



where [C] is a cation and [A] is an anion;

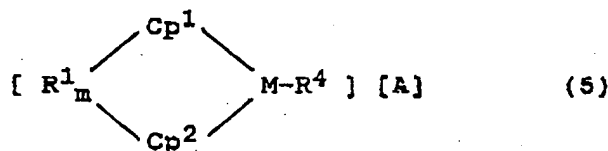
the catalyst system further containing a boron compound (D) represented by the general formula (4) below:



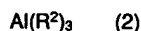
where each of the R^3 groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, or an aryl group, in an amount of from 0.01 mol to 0.8 mol per mol of the metallocene compound (A).

10. A catalyst for polymerization of an olefin, which comprises an ionic metallocene compound (a), and an organoaluminum compound (b) as catalyst components:

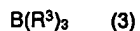
the ionic metallocene compound (a) being represented by the general formula (5) below:



where Cp^1 , and Cp^2 are independently a substituted or unsubstituted cyclopentadienyl group; R^1 is an alkylene group having 1 to 20 carbons, a dialkylsilylene group, a dialkylgermylene group, an alkylphosphindiy group, or an alkylimino group, R^1 crosslinking Cp^1 and Cp^2 ; m is 0 or 1; R^4 is an alkyl group or an aryl group; M is titanium, zirconium, or hafnium; and [A] is an anion; and the organoaluminum compound (b) being represented by the general formula (2):



where each of the R^2 groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, or an aryl group, and at least one of the R^2 group is an alkyl group; the catalyst system further containing a boron compound represented by the general formula (3) below:



where each of the R^3 groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, or an aryl group, in an amount of from 0.01 mol to 0.8 mol per mol of the ionic metallocene compound (a).



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 10 8294

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	WO-A-9 114 713 (EXXON CHEMICALS PATENTS INC.) * claims 1,11 * * examples 1-4 * ---	1,4,6, 8-10	C08F10/00 C08F4/646
A	DIE MAKROMOLEKULARE CHEMIE, RAPID COMMUNICATIONS vol. 13, May 1992, BASEL pages 277 - 281 , XP266808 PELLICHIA 'Polymerization of ethylene and propene in the presence of organometallic compounds of titanium and zirconium activated with tris(pentafluorophenyl)boron' runs 8, 10, 11,13,15,16 ---		
A	RAPRA ABSTRACTS vol. 14, no. 25, 5 December 1977, NØ 7705114L BEIKHOL 'Polymerization of ethylene in ethyl chloride over complex catalyst system modified by acids and Lewis bases' * abstract * -----		
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C08F
Place of search THE HAGUE		Date of completion of the search 07 SEPTEMBER 1993	Examiner FISCHER B.R.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- A : member of the same patent family, corresponding document	